

very steady state by the time the final experiments were made. In all cases some irregularity took place when new knife-edges were used, due no doubt to the wearing off of some slight "burr" left on the edge during sharpening.

The pendulum was sensitive to sudden variations of the weather. It would be a great advantage to enclose the apparatus in a case kept at constant temperature and pressure. A somewhat improved method of removing and replacing the bob is also desirable.

In conclusion, the writer wishes to express his best thanks to Prof. Sir J. J. Thomson for his unfailing kindness throughout the course of this investigation.

On the Spontaneous Crystallisation and the Melting and Freezing Point Curves of Mixtures of Two Substances which form Mixed Crystals and possess a Minimum or Eutectic Freezing Point.—Mixtures of Azobenzene and Benzyaniline.

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The behaviour of mixtures of naphthalene and β -naphthol has already been investigated, and the freezing and melting point curves and the curve of

spontaneous crystallisation for these mixtures described.* These substances were found to form a continuous series of mixed crystals, on a curve of Roozeboom's Type 1, the melting and freezing points of all the mixtures lying between the melting points of the pure substances.

The behaviour of mixtures of monochloroacetic acid and naphthalene was also investigated,† for it was stated by Cady‡ that these substances form mixed crystals of Roozeboom's Type 5, whose melting and freezing point curves exhibit a minimum or eutectic freezing point. Experiments were therefore made with these substances with the object of determining the form of the curve of spontaneous crystallisation, or supersolubility curve, for mixtures of this type. No sign of the formation of any mixed crystals was observed, however, in a lengthy series of experiments, and it was shown that naphthalene and monochloroacetic acid give the ordinary V-shaped freezing point curve for the solutions of two substances in each other, similar to that already obtained for mixtures of salol and betol.§ the only new feature being introduced by the existence of three modifications of monochloroacetic acid. The monochloroacetic acid and naphthalene mixtures having thus failed as an example of mixed crystals possessing a minimum or eutectic freezing point, another attempt was made to obtain a pair of substances with convenient melting points which form mixed crystals and possess the melting and freezing point curves with minimum eutectic point characteristic of Roozeboom's Type 5.

Azobenzene and benzylaniline were chosen for this purpose, and the present paper deals with mixtures of these substances.

CRYSTALLINE FORM OF BENZYLANILINE AND AZOBENZENE.

Benzylaniline, $\text{C}_6\text{H}_5\text{CH}_2\text{NH C}_6\text{H}_5$, has been described by Jaeger,|| who obtained transparent colourless crystals from a solution in methyl alcohol.

He found the crystals to be monoclinic, with axial ratios—

$$a : b : c = 2.1076 : 1 : 1.0948,$$

and

$$\beta = 76^\circ 36\frac{1}{2}'.$$

The habit is elongated along the b -axis, the plane of the optic axes being (010). The axial dispersion is strong, with $\rho > v$.

Azobenzene, $\text{C}_6\text{H}_5\text{NNC}_6\text{H}_5$, has been described by Boeris,¶ and by Calderon.**

* 'Journ. Chem. Soc.,' 1908, vol. 93, 1, p. 927.

† 'Phil. Trans.,' 1909, A, vol. 209, p. 337.

‡ 'Journ. Phys. Chem.,' 1899, vol. 3, p. 127.

§ 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 322.

|| 'Zts. für Kryst.,' 1907, vol. 42, p. 265.

¶ 'Zts. für Kryst.,' 1901, vol. 34, p. 301.

** 'Zts. für Kryst.,' 1880, vol. 4, p. 234.

The former obtained tabular orange-coloured crystals of azobenzene, from a solution in acetic ether, which he describes as monoclinic, with axial ratios—

$$a : b : c = 2.1076 : 1 : 1.3312,$$

and

$$\beta = 65^{\circ} 34'.$$

The plane of the optic axes is perpendicular to (010), and nearly parallel to (001), and there is considerable axial dispersion, $\rho < v$. Jaeger* points out that, although it is possible by a suitable choice of parametral faces to obtain similar axial ratios for the crystals of benzyaniline and azobenzene,

$$(\text{Azobenzene} \dots a : b : c = 2.1076 : 1 : 1.4220, \beta = 76^{\circ} 32')$$

$$\text{Benzyaniline} \dots a : b : c = 2.1076 : 1 : 1.6422, \beta = 76^{\circ} 36'),$$

yet this would require an unnatural position for the crystals, involving high indices for some of the forms observed, so that the relation between the two substances is a somewhat distant one.

Jaeger† gives the melting points of pure azobenzene and benzyaniline as 68° and 36.5° . He also gives the melting points of a few mixtures of these substances, which he states form mixed crystals and show a minimum eutectic point. He obtained mixed crystals of azobenzene and benzyaniline from solution in alcohol and chloroform as small red needles, which were strongly pleochroic, but unsuitable for crystallographic investigation.

Calderon‡ gives the melting point of azobenzene as 66.5° , while Pickering§ gives 66.8° .

Mixtures of azobenzene and benzyaniline have also been investigated by Bruni and Gorni|| and by Garelli and Calzolari;¶ these authors do not, however, give any melting points for actual mixtures, but state that azobenzene and benzyaniline form mixed crystals, and exhibit abnormal cryoscopic behaviour.

MICROSCOPIC EXAMINATION OF AZOBENZENE AND BENZYLANILINE CRYSTALLISED FROM FUSION.

In the present investigation azobenzene and benzyaniline were first examined under the microscope as a thin film crystallised from fusion on a microscope slide under a cover glass.

* *Loc. cit.*

† ‘Zts. für Kryst.,’ 1907, vol. 42, p. 265.

‡ ‘Zts. für Kryst.,’ 1880, vol. 4, p. 234.

§ ‘Phil. Mag.,’ (5), 1895, vol. 39, p. 510.

|| ‘Real. Accad. dei Lincei,’ 1899, vol. 8, pp. 454 and 470.

¶ ‘Real. Accad. dei Lincei,’ 1899, vol. 8, p. 579, and ‘Gazetta,’ vol. 29, ii, p. 259.

Azobenzene appears as stout radiating prisms and irregular plates of a fine orange colour. The plates and most of the prisms are strongly pleochroic, the colours being orange and yellow. The extinction of the prisms is usually straight or nearly so, but on some it is oblique with angles ranging to about 35° . Many of the prisms do not become dark at all, but show a strong red and green coloration about the position of extinction, owing to strong dispersion of the optic axes. With convergent light, some of the prisms with straight extinction show an interference figure resembling that of brookite, with a positive acute bisectrix in the centre of the field. The optic axial plane is parallel to the length of the prisms, and the dispersion $\rho < v$, the crystals being nearly uniaxial for red light. The plates commonly show, in sodium light, hyperbolic bands indicating the slightly oblique emergence of an obtuse bisectrix or third mean line.

These appearances agree with the description of the crystals given by Boeris,* the prismatic outlines being due to a vertical or oblique position of the thin tabular crystals.

Benzylaniline, examined in the same way, showed stout colourless blades growing radially from centres, with approximately straight extinction. In convergent light the needles show a wide angle negative bisectrix, nearly central, the axial plane being perpendicular to the length of the needles. In some of the needles a single optic axis is visible at the edge of the field.

The plates and needles of azobenzene and benzyaniline obtained from fusion on the microscope slide rarely possess angles measurable under the microscope, their edges being rounded or ragged.

Crystals formed in drops of azobenzene dissolved in benzene or alcohol were also examined under the microscope. They were rhombs with an angle of 49° and diagonal extinction. Viewed in convergent light these rhombs showed an obtuse bisectrix or third mean line.

Drops of benzyaniline dissolved in toluene or ether gave needles with angle of 72° approximately, the extinction being always parallel to the length of the needles. Viewed in convergent light these needles showed a normally emergent bisectrix, both optic axes being visible.

MIXTURES OF AZOBENZENE AND BENZYLANILINE.

Mixtures of azobenzene and benzyaniline were next investigated, and the freezing and melting point curves for these mixtures were determined.

* *Loc. cit.*

The Freezing Point Curve.

To obtain the freezing point curve the mixtures varying in concentration from 100 per cent. azobenzene to 100 per cent. benzylaniline were enclosed in sealed glass tubes. Each mixture was heated in a water bath until it was completely melted, with the exception of one or two small crystals at one end of the tube. These crystals were watched with a lens as the temperature of the bath was lowered, until a temperature was reached at which equilibrium was found to exist between them and the liquid mixture. This temperature, at which the crystals neither grew nor dissolved, was taken as the freezing point of the mixture. This method has been fully described.*

The results obtained appear tabulated below :—

Percentage composition of mixture.		Freezing point.	Percentage composition of mixture.		Freezing point.
Azobenzene.	Benzylaniline.		Azobenzene.	Benzylaniline.	
100	0	66	19·972	80·028	27
90·025	9·975	62·5	19·122	80·878	26·5
88·61	11·39	61·5	17·958	82·042	27
80·076	19·924	58	15·579	84·421	29
70	30	53·5	15	85	28·5
59·81	40·19	48	10·437	89·563	31
50	50	42·6	5·187	94·813	33
40	60	35	5·018	94·982	33
34·8	65·2	33	2·506	97·494	34·5
29·868	70·132	30·5	0	100	35·5
20·054	79·946	27			

These freezing points, when plotted on the concentration-temperature diagram, give the ordinary V-shaped freezing point curve, with a minimum or eutectic point at 26·5° for the mixture 81 per cent. benzylaniline, 19 per cent. azobenzene.

On the side which shows excess of benzylaniline this curve is almost a straight line, but on the side showing excess of azobenzene the curve is slightly concave towards the concentration axis.

The Melting Point Curve.

To obtain the melting point curve the same tubes were used as in the experiments on the freezing point curve. The tubes containing the various mixtures were heated in turn and shaken until the crystals had completely melted. Each tube was then cooled, and the liquid mixture allowed to

* 'Journ. Chem. Soc.,' 1908, vol. 93, 1, p. 931.

solidify completely. As with all substances forming mixed crystals, the solid first deposited differs in composition from the original liquid, and as the temperature continues to fall, different mixed crystals form, whose composition approximates more and more nearly to that of the original liquid, until the very last mixed crystals that form should have the exact composition of the original liquid taken. Crystals of this composition, therefore, have a lower melting point than any of those previously deposited.

When the mixture was completely solid the tube was immersed in a cold water bath, the temperature of which was raised very slowly while the solid mixture was watched carefully with a lens. At first the mixture is quite compact and solid, but when the temperature has been raised to a certain point some of the crystals are seen to begin to melt; parts of the mixture appear slightly sticky; and, on further raising the temperature very slightly, if the tube be inverted a little liquid stream starts running down the sides. This point is taken as the melting point of a mixture whose composition is the same as that of the original liquid taken. The melting point curve thus obtained agrees very approximately with some later experiments described on pp. 352-4, in which the melting point curve was obtained directly by analysis of the mixed crystals.

Each experiment was repeated several times, and the temperature at which melting was first observed was very carefully noted. All the melting points are thus determined with rising temperature, the following being the tabulated results:—

Percentage composition of mixture.		Melting point.	Percentage composition of mixture.		Melting point.
Azobenzene.	Benzylaniline.		Azobenzene.	Benzylaniline.	
100	0	66	19·972	80·028	26
90·025	9·975	54	19·122	80·878	26
80·076	19·924	46	17·958	82·042	26
70	30	42	15·579	84·421	26
59·81	40·19	37	15	85	26
50	50	32·4	10·437	89·563	26
49·92	50·08	32·5	5·187	94·813	26
40	60	29	5·018	94·982	26
34·8	65·2	26	2·506	97·494	26
29·868	70·132	26	0	100	35·5
20·054	79·946	26			

When plotted on the concentration-temperature diagram these points give the complete melting point curve for all mixtures of azobenzene and benzylaniline. As will be seen from the diagram, part of the melting

point curve is flat, and runs parallel to the concentration-axis, and mixtures of all concentrations between 35 per cent. azobenzene 65 per cent. benzylaniline, and 2.5 per cent. azobenzene 97.5 per cent. benzylaniline, start melting at the same temperature, viz., 26° . Hence, no mixed crystals are deposited on the side of the eutectic weak in azobenzene, but only pure benzylaniline, which grows as soon as the temperature given by the freezing point curve is reached, until the mixture reaches the eutectic composition, when the rest of the liquid solidifies as a mixture of pure benzylaniline with the mixed crystals containing 35 per cent. azobenzene and 65 per cent. benzylaniline, whose melting point is 26° . This result is confirmed by the microscopic examination of the solidified mixtures as described below (p. 354). On the other side of the eutectic, however, in mixtures containing excess of azobenzene, a series of mixed crystals are formed which contain from 100 per cent. to 35 per cent. of azobenzene. As has been shown above (p. 348) a mixture of approximately 81 per cent. benzylaniline 19 per cent. azobenzene freezes at 26.5° , where the curve exhibits a eutectic point. A mixture of this composition, therefore, melts and freezes very approximately at the same temperature. This is the invariant point, and on either side of it different solids exist in equilibrium with the liquid. At this point four phases can co-exist, namely, mixed crystals containing 35 per cent. of azobenzene, pure benzylaniline, liquid solution, and vapour.

The melting point curve was not at first obtained in the form here described. In the first experiments, the flat part of the curve which extends from 65 to 100 per cent. of benzylaniline, appeared only to extend from 65 to 85 per cent. of benzylaniline. Mixtures containing between 85 and 97.5 per cent. benzylaniline, which were allowed to solidify spontaneously in a sealed tube and were then reheated, appeared to start melting at temperatures varying from 27° to 33° , instead of at 26° , as subsequently found. As originally plotted, therefore, the melting point curve pointed to the existence of two series of mixed crystals, one on each side of the eutectic. Further careful experiments showed, however, that mixed crystals do not really separate on the side of the eutectic containing excess of benzylaniline, but pure benzylaniline only.

Experiments made under the microscope by examining the crystals growing from drops of these mixtures on a slide, showed that the first crystals separating from mixtures containing more than 81 per cent. of benzylaniline are pure white in colour, and show no trace of the orange colour of the azobenzene, and are therefore probably pure benzylaniline. But, if pure benzylaniline only is first deposited from these mixtures until the eutectic composition is reached, the remaining liquid will solidify as a mixture of

pure benzylaniline with mixed crystals of composition 35 per cent. azobenzene 65 per cent. benzylaniline. All these mixtures, therefore, since they contain some proportion of mixed crystals of this composition, should start melting at 26° . As has been stated, this melting point was not at first noticed; but, in some later experiments, it was found that if the tubes containing the mixtures with 2.5, 5, and 10 per cent. of azobenzene were melted so as to leave a few small crystals in the tube, and then allowed to solidify slowly at not too low a temperature, on heating these tubes again a slight melting does occur at 26° . On the other hand, if these same tubes are heated until the mixtures are completely liquid, and are then cooled and shaken till they crystallise spontaneously at a low temperature, no melting can be detected at 26° , but only at from 27° to 33° .

This discrepancy may, perhaps, be due to the fact that in the latter case the mixtures have crystallised spontaneously in the tubes at temperatures considerably lower than their freezing points. The pure benzylaniline may have formed so suddenly and rapidly that the eutectic composition is overshoot, so much benzylaniline coming out of solution that the remaining liquid contains a higher percentage of azobenzene than the eutectic, and consequently forms mixed crystals containing more than 35 per cent. azobenzene, which have higher melting points than 26° . When, however, the same mixtures are allowed to solidify slowly after inoculation with benzylaniline, as stated above, the true melting point 26° is obtained. In connection with this point it may here be mentioned that it was found possible later on, in some experiments described below, to separate the very first crystals which formed spontaneously in the mixtures of azobenzene and benzylaniline containing small percentages of azobenzene. If pure benzylaniline is first deposited from these mixtures, the melting point of the crystals which first form should be 35.5° , the melting point of the pure benzylaniline. It was found that the crystals thus separated from all mixtures on the benzylaniline side of the eutectic, after being washed with benzene to get rid of the mother liquor, all melt at 35.5° . Thus the first crystals forming spontaneously from all these mixtures have the melting point of pure benzylaniline, and consequently no mixed crystals are formed on this side of the eutectic, but crystals of pure benzylaniline only, in the usual manner of mixtures of two substances which yield the ordinary V-shaped melting point curve.

In the experiments made to determine the freezing point curve, the mixtures were enclosed in sealed glass tubes, and the temperature of equilibrium was obtained between the liquid and a few small crystals of unknown constitution. If no mixed crystals are formed on the side of the eutectic showing excess of benzylaniline, the freezing point curve on this

part of the diagram must be the equilibrium curve between the liquid mixture and pure benzylaniline. This was proved to be true by some further experiments, in which mixtures containing 5, 10, and 15 per cent. of azobenzene were placed in open test tubes, immersed in a water bath and inoculated with a minute crystal of benzylaniline.

The equilibrium points so obtained were found to agree with the freezing point curve obtained above.

The Melting Point Curve Obtained by Analysing the Mixed Crystals.

The method of experimenting described above for obtaining the melting point curve appears to be somewhat rough and unsatisfactory; in order, therefore, to check and confirm this curve, the melting points of mixed crystals of known composition were determined as follows:—

Mixtures of azobenzene and benzylaniline of various compositions were dissolved in benzene in a beaker, and the liquid was stirred regularly by means of a water motor while the benzene evaporated slowly. The liquid was inoculated with a minute mixed crystal, and as evaporation proceeded a crop of small crystals in equilibrium with the solution was slowly deposited and whirled about in the liquid. When a sufficient quantity of crystals had formed, the solution was filtered off by means of an air pump, and the crystals obtained dry on the filter in a small platinum cone. The crystals were then powdered in a mortar and placed in an exhausted desiccator for several hours to dry off the last traces of benzene. Since these crystals represent a small crop grown from, and in equilibrium with, a comparatively large volume of solution, they may be taken to be very approximately homogeneous. If this is so, when placed in a capillary tube they will melt at an approximately constant temperature, and this was found to be usually the case. When the temperature was not quite constant, but extended through a range of 1° or 2° , the mean was taken to represent the true melting point. The melting point for any crop being ascertained, the crystals were next analysed in order to find their composition. The analysis was carried out by extracting the benzylaniline from a known weight of the crystals with dilute hydrochloric acid, the azobenzene being left undissolved.

Three extractions in warm acid were found sufficient to dissolve all the benzylaniline, and the pure azobenzene left behind was dried and weighed. In this manner the composition of the original crystals was obtained.

These experiments were repeated with a considerable number of different solutions of azobenzene and benzylaniline in benzene, each solution giving a different set of homogeneous mixed crystals. From these experiments it

is possible, therefore, to plot the melting point curve for the azobenzene-benzylaniline mixtures, since the composition and melting point of each homogeneous crop of mixed crystals are known.

The following are the details of these experiments:—

Mean melting point of mixed crystals grown from solution in benzene.	Percentage composition found by analysis.		Mean melting point of mixed crystals grown from solution in benzene.	Percentage composition found by analysis.	
	Azobenzene.	Benzylaniline.		Azobenzene.	Benzylaniline.
60	93·893	6·107	37·75	57·57	42·43
59·6	94·23	5·77	37	55·4	44·6
56·9	93·33	6·67	35·5	56·95	43·05
48·1	83·32	16·68	33·5	54·64	45·36
40·8	66·07	33·93	30·25	46·5	53·5

These results, when plotted on the concentration-temperature diagram, should give the melting point curve for the azobenzene-benzylaniline mixtures, each set of crystals giving a point on the curve. These points are all shown on the diagram by $\oplus$. It will be seen that some of these points lie slightly above the melting point curve originally obtained, though, on the whole, the new experiments may be considered to confirm the original curve fairly well. The later experiments seem to show, however, that the melting point curve, as plotted from the original experiments, is slightly too low. This result might have been expected from a consideration of the method employed, for it was assumed that the last drop of the liquid to solidify gives crystals having the original constitution of the liquid. This would, no doubt, be the case if the cooling of the liquid were sufficiently slow, so that as the mixed crystals grew there was sufficient time for the equilibrium to be maintained by a continuous readjustment between the crystals and the liquid. But if the cooling is not sufficiently slow it is probable that the readjustment is incomplete, so that the last mixed crystals formed contain a slightly larger percentage of benzylaniline than the original mixture. These crystals would, therefore, have a slightly lower melting point than those having the composition of the original liquid. The later experiments, in which the mixtures were analysed, tend to show that this is the case, although the discrepancy is very slight, and does not appear to amount to more than approximately 1° of temperature.

The melting points for azobenzene and benzylaniline obtained above are 66° and $35\cdot5^{\circ}$. On comparing these values with those previously obtained,

it will be seen that they are slightly lower than Jaeger's values 68° and 36.5° , and agree more nearly with those of Calderon and Pickering, who give the melting point of azobenzene as 66.5° and 66.8° respectively. The slightly lower values obtained in these experiments would seem to indicate that in all probability some small amount of impurity exists in the substances used in this research.

We may also compare the melting points obtained by Jaeger for the few mixtures of azobenzene and benzylaniline he examined with those obtained above. Jaeger's values are :—

Percentage composition of mixture.		Melting point.
Azobenzene.	Benzylaniline.	
6.5	93.5	35
12	88	32.5
51.4	48.6	49
76.3	23.7	61.5

It will be seen that these values for the melting points are considerably higher than those indicated by the diagram.

Microscopic Examination of Mixtures of Azobenzene and Benzylaniline Crystallised from Fusion.

A great number of drops of different mixtures were allowed to crystallise on the microscope slide at the temperature of the surrounding air, and the crystals were examined as they grew.

Various mixtures, containing 10, 20, 30, 35, 40, and 60 per cent. of azobenzene, were examined in this way.

The crystal needles first forming in the 10 per cent. mixture were colourless, and some colourless crystals also appeared in the 20 per cent. mixture. The remaining mixtures gave only coloured needles. The crystal needles were always formed with their oblique ends rounded or ragged, so that it was impossible to measure their angles, and when the liquid drop has completely solidified they form a confused mass intersecting each other in all directions. In all the mixtures the extinction was either straight or inclined at 1° or 2° to the length of the needles. Crystals grown from mixtures containing up to 30 per cent. azobenzene, when viewed in convergent light, usually showed both optic axes with the bisectrix nearly normal, although some of the needles showed only one optic axis on the edge of the field.

Needles grown from mixtures containing over 30 per cent. azobenzene always showed one optic axis only on the edge of the field. The axial plane always appears to be nearly perpendicular to the length of the crystal needles. That the colourless crystals which first appear in the mixtures weak in azobenzene are pure benzyaniline, is indicated by their optical properties.

The coloured crystals in the other mixtures are probably mixed crystals of various compositions. Some of these mixtures containing the larger proportions of azobenzene are very viscous, and remain partly liquid under a cover glass at the temperature of the room long after crystallisation has first started on the microscope slide.

Although these experiments were repeated several times, the results obtained do not appear to lead to very definite conclusions, the crystal needles being always ill-formed, with ragged edges. The temperature at which the needles grew on the slide was about 14° or 15° , so that it was considerably lower than the temperature at any point of the freezing point curve. The conditions of growth are therefore quite different, and at these lower temperatures the composition of the crystals separating from any liquid drop may differ from the composition of crystals separating from a similar drop at temperatures between the freezing and melting point curves determined above.

The Supersolubility Curve, or Curve of Spontaneous Crystallisation.

The freezing and melting point curves for mixtures of azobenzene and benzyaniline having been determined, an attempt was next made to plot the curve of spontaneous crystallisation for these mixtures, as has already been done for mixtures of naphthalene and β -naphthol.

Two methods of experimenting were employed, both of which have been used in the previous researches with Prof. Miers on spontaneous crystallisation, viz.: (1) the method of sealed tubes; (2) the measurement of the refractive indices of cooling mixtures.

(1) *Experiments with Sealed Tubes.*—Azobenzene, benzyaniline, and their mixtures were enclosed in sealed glass tubes which also contained some angular fragments of corundum to ensure friction.

The tubes containing the various mixtures were then heated in a water bath with frequent shaking until all the crystals had completely melted.

The water bath was then allowed to cool slowly, and as the temperature fell the tubes were shaken continuously, either by hand or on a rocking apparatus placed within the water bath. With each mixture it was found that when the temperature had fallen to a certain point, a dense shower of crystals suddenly appeared in the tube and the whole mixture rapidly

became solid. The temperature at which the shower occurs depends upon the composition of the mixture, and was found to be approximately constant for each mixture.

The experiment with each tube was, in general, repeated several times; the following table gives all the results obtained from 16 tubes treated in this manner:—

Percentage composition of mixture in tube.		Temperature of spontaneous crystallisation.
Azobenzene.	Benzylaniline.	
100	0	58°·5, 56°·5.
90·025	9·975	51°, 51°·5, 51°·5, 52°·2.
79·96	20·04	48°·5, 48°·5, 48°·5, 48°.
70	30	43°·5, 43°, 42°, 42°.
59·81	40·19	39°·6, 39°·5, 39°·5, 38°·5, 38°·5.
49·92	50·08	35°·5, 34°, 34°·7, 35°·2, 35°·5, 35°·5.
39·80	60·20	28°, 30°, 30°, 30°, 30°.
34·80	65·20	26°, 26°, 26°.
29·868	70·132	22°.
19·972	80·028	17°·5, 18°·5, 18°·4, 18°·4, 18°.
17·958	82·042	18°, 16°·2, 18°, 18°, 18°.
15·579	84·421	18°, 18°·1, 18°·2.
15	85	18°.
10·437	89·563	20°·5.
5·187	94·813	26°·5, 26°.
0	100	30°.

These results, when plotted on the concentration-temperature diagram, give the complete supersolubility curve, or curve of spontaneous crystallisation, for azobenzene, benzylaniline, and their mixtures. Where there was a slight variation in the temperature of spontaneous crystallisation of a single tube, the highest temperature obtained has been always taken as the true temperature of spontaneous crystallisation; in the other experiments the mixture must have passed slightly into the labile state, probably in consequence of too rapid cooling.

This curve, which is shown on the diagram, separates the metastable and labile areas for all mixtures of azobenzene and benzylaniline. Above this curve the mixed crystals cannot form spontaneously, although they will grow after inoculation, but below it mixed crystals can, and do, form spontaneously in a shower. As will be seen from the diagram the supersolubility curve runs roughly parallel to the freezing point curve. On the left hand side of the eutectic composition it crosses the melting point curve twice, and on the right hand side of the eutectic it again crosses the melting point curve. Near the eutectic composition the supersolubility curve reaches a minimum, and for mixtures containing from 70 to 90 per cent. of benzylaniline the

supersolubility curve is very flat, the temperatures of spontaneous crystallisation for these mixtures only varying by about 2°.

(2) *The Refractive Indices of Mixtures.*—An attempt was now made to verify the supersolubility curve just obtained by observing the sudden change in the index of refraction which takes place on the curve. This method has been used before to obtain the supersolubility curve for mixtures of salol and betol and for various aqueous solutions of salts, &c.*

The liquid mixtures were heated and placed in the trough of the inverted goniometer and their refractive indices were determined as they cooled by the method of total reflection within a dense glass prism immersed in the liquid.

With the aqueous solutions examined in this manner it was found that the refractive index rose steadily till the labile temperature was reached. Here a dense shower of crystals occurred, which soon settled at the bottom of the goniometer trough, the refractive index afterwards falling continually as the temperature fell.

The mixtures of azobenzene and benzylaniline were examined in this manner from the time when the warm mixture was first placed in the trough until the dense shower occurred at the labile temperature. As with the mixtures of salol and betol already examined, it was almost impossible to determine the refractive index beyond this point owing to the density of the shower, the crystals remaining suspended in the liquid instead of sinking to the bottom of the trough as with the aqueous solutions of salts, and thus rendering the mixtures almost opaque.

The mixtures of azobenzene and benzylaniline examined contained from 50 to 100 per cent. of benzylaniline. In these it was found that the index rose gradually and regularly as the temperature fell, until the dense labile shower of crystals occurred. Mixtures containing more than 50 per cent. of azobenzene were not examined, as they were somewhat viscous, and consequently intense concentration streams arise, which cause irregularities in the index-temperature curves, and also because their high temperatures of spontaneous crystallisation render them unsuitable for use in the goniometer trough. As the mixtures cooled in the trough they were stirred continually by means of a small platinum vane driven by an electric motor.

The liquid mixtures being somewhat deep red in colour, it was found that the monochromatic light of the sodium flame was nearly absorbed, and that the edge of the shadow denoting total internal reflection could hardly be seen. White light was therefore used to illuminate the prism, and a piece of

* 'Roy. Soc. Proc.' 1907, A, vol. 79, p. 322; 'Journ. Chem. Soc.' 1908, vol. 93, i, p. 384.

red glass was held in front of the eye-piece of the telescope to cut off light of other colours. The refractive index of the liquid mixtures is thus determined for red light. The shadow denoting total internal reflection obtained in this way is quite sharp and distinct. The shower of crystals occurring in the mixtures at the labile temperature is always accompanied by a considerable rise in temperature. The following are the general results of the experiments on the refractive indices of mixtures of azobenzene and benzyaniline.

Experiment 1.—Azobenzene = 50 per cent.
Benzyaniline = 50 „

The index rose from 1·62022 at 61° to 1·63237 at 35°. A dense shower occurred at 35° and the temperature rose to 38°.

Experiment 2.—Azobenzene = 47·5 per cent. approx.
Benzyaniline = 52·5 „ „

The index rose from 1·61684 at 63° to 1·63146 at 35°. A dense shower occurred at 33·5°, the temperature rising to 38°.

Experiment 3.—Azobenzene = 45 per cent. approx.
Benzyaniline = 55 „ „

The index rose from 1·61432 at 66° to 1·63115 at 33°. A very dense shower occurred at 32°, the temperature rising to 36°.

Experiment 4.—Azobenzene = 39·995 per cent.
Benzyaniline = 60·005 „

The index rose from 1·61421 at 60° to 1·62941 at 31°. A shower of crystals occurred at 31° and the temperature rose to 33°.

Experiment 5.—Azobenzene = 35 per cent.
Benzyaniline = 65 „

The index rose from 1·61224 at 61° to 1·62864 at 27°. A shower of crystals occurred at 26·5 and the temperature rose to 28·5.

Experiment 6.—Azobenzene = 30 per cent.
Benzyaniline = 70 „

The index rose from 1·61202 at 55° to 1·62937 at 22°. A slight shower began to form spontaneously at 22° and became gradually denser without change of temperature.

Experiment 7.—Azobenzene = 30 per cent. approx.
Benzyaniline = 70 „ „

The index rose from 1·61054 at 60° to 1·62892 at 22°. A shower of crystals occurred at 22° and the temperature rose to 25°.

Experiment 8.—Azobenzene = 25 per cent.
Benzyaniline = 75 „

The index rose from 1·60946 at 56° to 1·62666 at 20·5. A shower occurred at 20·5, the temperature rising to 25° and the index falling. At 21° the index had fallen to 1·62627.

Experiment 9.—The same mixture was used as in Experiment 8. The index rose from 1.61174 at 53° to 1.62622 at 21°. A dense shower occurred at 20°·5, but no more readings for the index were possible. The temperature rose to 24°·5.

Experiment 10.—Azobenzene = 20.045 per cent.
 Benzy laniline = 79.955 „

The index rose from 1.60544 at 58° to 1.62566 at 19°. A shower of crystals occurred at 19° and the temperature rose to 25°. The index fell again during the shower and reached 1.62397 at 21°·5.

Experiment 11.—Azobenzene = 17.256 per cent. approx.
 Benzy laniline = 82.744 „ „

The index rose from 1.60653 at 56° to 1.62428 at 18°·2. A dense shower of crystals occurred at this temperature and no more readings were possible. The temperature rose to 27°.

Experiment 12.—Azobenzene = 14.886 per cent.
 Benzy laniline = 85.114 „ „

The index rose from 1.61060 at 44° to 1.62282 at 18°·2. A shower of crystals occurred at this temperature and the index fell with rise of temperature, reaching 1.62165 at 23°.

Experiment 13.—Azobenzene = 10.003 per cent.
 Benzy laniline = 89.997 „ „

The index rose from 1.60235 at 57° to 1.61895 at 21°. A dense shower occurred at 21°, the temperature rose to 29° and the index fell to 1.61866 at this temperature.

Experiment 14.—Azobenzene = 0 per cent.
 Benzy laniline = 100 „ „

The index rose from 1.59324 at 64° to 1.60999 at 29°·2. Crystals first appeared at 30° and a dense shower occurred at 29°·2, the temperature then rising to 35°.

From experiments 1, 4, 5, 6, 8, 10 and 13, in which the exact composition of the mixtures is known, it is possible to ascertain the refractive index of any given mixture at any temperature. The results of all these experiments, taken together, may be expressed by curves drawn with concentrations as abscissæ and temperatures as ordinates, the refractive index being constant for each curve. Such curves were drawn for the following values of index:—1.608, 1.610, 1.612, 1.614, 1.616, 1.618, 1.620, 1.622, 1.624, 1.626, 1.628, 1.630. They were found to be very approximately straight lines, equidistant and parallel to each other, and inclined to the concentration axis at an angle of 50°, the scale chosen being such that 10 per cent. on the concentration axis corresponds to 8° on the temperature axis. Now, if a line be drawn on the concentration-temperature diagram perpendicular to these lines of constant index, and, therefore, inclined at an angle 40° to the concentration axis, the refractive

index of any mixture, as it cools, may be measured along this line just as the temperature is measured along the vertical axis.

The curves of constant index are shown on the diagram, and from these it is possible to plot the whole series of observations of refractive indices obtained in the above experiments. (See p. 363.)

These experiments give a number of curves, numbered 1 to 14 on the diagram, the number of the curve corresponding to the number of the experiment. The curves show slight irregularities, especially at high temperatures. These irregularities are probably due to concentration-streams, which are particularly marked when the liquid mixture is first introduced into the goniometer trough.

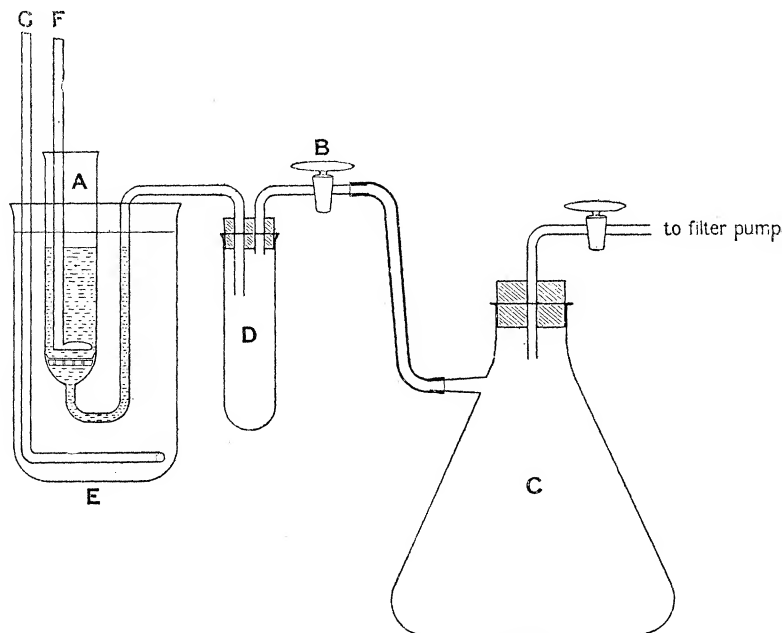
On the whole, however, the curves go straight down the diagram and show very little variation in concentration as the mixtures cool, until the labile shower occurs at points which lie very approximately on the supersolubility curve already obtained by the method of sealed tubes. These results, obtained from the refractive indices of the mixtures, therefore confirm those already obtained from the experiments with sealed tubes, by which the position of the supersolubility curve was first established. In two or three of the experiments, in which it was possible to trace the refractive index after the labile shower had begun, it was found that the index attained a maximum value on the supersolubility curve and then fell again with rise of temperature and approached the freezing point curve. This behaviour is seen in experiments 10, 12 and 13. In general, however, it is not possible to trace the change of index with any certainty after the shower has occurred, the shower being usually so dense as to render the mixture opaque.

The crystals which first separate from the mixtures during the showers were examined from time to time under the microscope, but no definite conclusions as to their nature could be drawn from the observations. The crystals were always needles and showed straight extinction. Their angles were never measurable under the microscope. An interference figure was usually visible; sometimes both optic axes were seen with the bisectrix normal, and sometimes only one optic axis was visible, surrounded by rings, the birefringence being always positive.

Nature of the Crystals Separating on the Supersolubility Curve.

The supersolubility curve having been determined by the above experiments, an attempt was now made to ascertain the composition of the crystals which first form spontaneously on the supersolubility curve for various mixtures. In order to do this for any mixture it is necessary to separate the first crystals which form in the labile shower.

For this purpose the following apparatus was devised by Prof. Bowman, and is shown in the figure:—



A wide tube A is drawn out at the lower end to form a U-tube, the end of which is bent again and passes through a cork into the tube D. This U-tube is immersed in a large water-bath E. Another tube passes through the cork of the tube D and connects it with the vacuum flask C and air pump. By means of the tap B this connection may be opened or closed at will. At the bottom of the tube A is a porcelain filter-plate covered with a filter-paper.

The liquid to be experimented upon is placed in the U-tube at a high temperature, the water-bath E having been previously heated. The liquid in the U-tube is stirred continuously and steadily by means of a plunging stirrer F, driven by an electric motor. By far the greater part of the liquid mixture is contained in the wide part A of the U-tube, and is allowed to cool very slowly in the water-bath. As soon as the liquid reaches the labile temperature a shower of crystals begins to form in the tube A. The tap B is then immediately turned and the liquid mixture sucked off into the tube D, leaving the first crystals that form in the shower dry and free from mother liquor upon the filter-paper in A. A thermometer was placed in the water-bath, which was kept stirred throughout the experiment by the glass stirrer G. The melting point of the crystals left in the tube A was then obtained

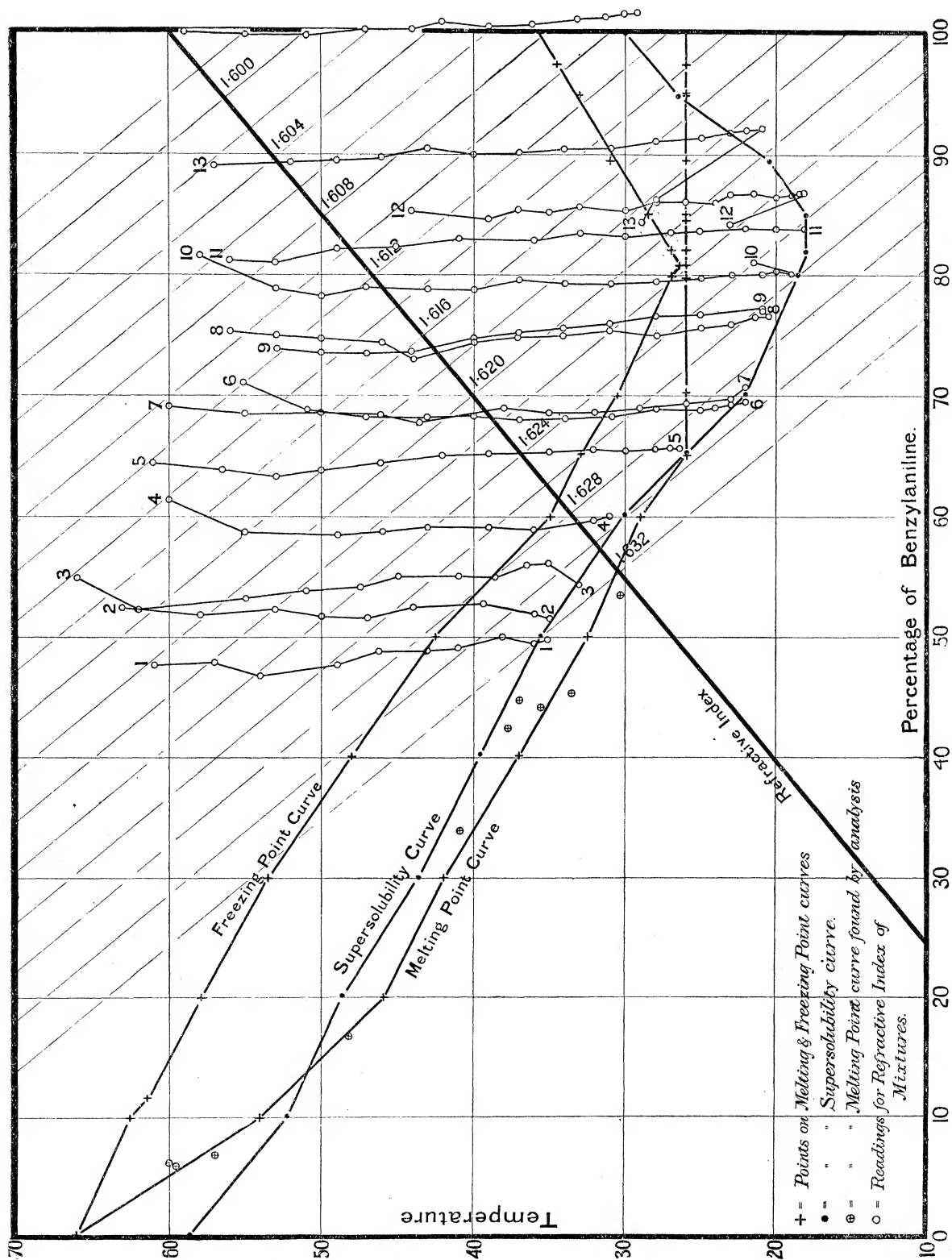
in a capillary tube attached to the bulb of a thermometer in the usual manner. The capillary tubes used in these experiments were examined from time to time under the microscope, by which means the first signs of melting at the edges of the crystals were easily detected.

It is necessary to catch the shower in the **U**-tube at once so as to separate the first crystals that form. If the tap B connecting the tube A with the vacuum flask is not turned immediately the first crystals appear, too much solid forms in A, and the filter-paper is left with a large mass of crystals on it, instead of only the first few crystals which form. Sometimes the liquid mixture solidifies at the narrow upper end of the **U**-tube when running off into D, and this prevents the mother liquor from being properly drawn away from the first crystals on the filter. Usually, however, if the mixture is very carefully watched, it is possible to isolate the first crystals of the labile shower, and though they are always extremely small and brittle needles they have clear sharp edges, and appear quite free from the mother liquor. The following results were obtained with this apparatus, the crystals being always examined in capillary tubes as stated above.

1. Mixture containing 40 per cent. benzyaniline ; 60 per cent. azobenzene. —This mixture was placed in the **U**-tube at about 80° and cooled slowly in the water-bath whilst it was stirred continuously. It crystallised spontaneously very suddenly at a somewhat high temperature, *i.e.* 39.5° , and it was found extremely difficult to draw off the mother liquor with sufficient rapidity to ensure the first crystals that formed being left clean on the filter. The experiment had therefore to be repeated several times before any definite result was obtained. At length, however, the liquid was drawn off, leaving a few of the very first crystals of the labile shower on the filter. When examined in a capillary tube these showed a definite melting point at 39° . The diagram shows that mixed crystals whose melting point is 39° have a composition of approximately 35 per cent. benzyaniline, 65 per cent. azobenzene. This, therefore, appears to be the composition of the crystals separating spontaneously from a liquid mixture containing 40 per cent. benzyaniline and 60 per cent. azobenzene.

Another experiment with the same liquid mixture yielded a larger crop of crystals on the filter. These appeared to be quite dry and free from mother liquor, but the melting point of different samples did not appear to be quite constant, the crystals melting at 39° , 38.5° , and 39.5° . The composition of these crystals would appear therefore to vary from 36 per cent. benzyaniline with 64 per cent. azobenzene, to 34 per cent. benzyaniline with 66 per cent. azobenzene.

2. Mixture containing 50 per cent. benzyaniline ; 50 per cent. azobenzene.



—This mixture was placed in the U-tube apparatus at 70° . A shower of crystals began to form at 35° , and the rest of the liquid was driven into the tube D leaving the first crystals of the shower dry on the filter. Three samples of these were examined in capillary tubes and found to melt at 34° , 35° , and 34.5° , and their composition therefore probably varies from 44.5 per cent. benzy laniline with 55.5 per cent. azobenzene, to 46.5 per cent. benzy laniline with 53.5 per cent. azobenzene. Mixed crystals of approximately this composition appear therefore to separate spontaneously from a liquid mixture containing 50 per cent. azobenzene with 50 per cent. benzy laniline.

3. Mixture containing 65 per cent. benzy laniline ; 35 per cent. azobenzene. —This mixture was placed in the U-tube at 70° and stirred steadily. A shower of crystals began to form at the labile temperature 26° , and the first crystals were easily separated, since in this mixture the shower does not form so suddenly throughout the liquid as is the case with mixtures containing a higher percentage of azobenzene. Three samples were examined in capillary tubes and found to melt at temperatures between 28° and 29° , their composition therefore varying from 59.5 per cent. benzy laniline with 40.5 per cent. azobenzene, to 61 per cent. benzy laniline with 39 per cent. azobenzene.

4. Mixture containing 75 per cent. benzy laniline ; 25 per cent. azobenzene. —This mixture was placed in the U-tube at 70° . At 20° a shower began to form in the tube. This was separated from the rest of the liquid and the crystals examined in capillary tubes. They were found to start melting at 26° . The capillary tubes must therefore contain some mixed crystals of constitution 65 per cent. benzy laniline, 35 per cent. azobenzene, which melt at 26° , and give the limit beyond which mixed crystals are not formed, the rest of the mixture in the capillary tubes being presumably pure benzy laniline. Another experiment was made with the same mixture by the same method. In this experiment it was noticed that the shower began to form at 20° with a very few small needle-shaped crystals and radial groups, and a thick shower did not come down immediately. These small crystals were separated in the usual way and washed with a few drops of benzene while still on the filter in the U-tube, the benzene being at once drawn off by means of the filter pump. They were then examined under the microscope and placed in capillary tubes. Some of them were pure white in colour, and some showed traces of the orange colour of the azobenzene. The colourless crystals in the capillary tubes when slowly heated in a water-bath showed no sign of melting till the temperature was raised to 35.5° , the melting point of pure benzy laniline. The crystals which showed some sign of the azobenzene colour, however, all began to melt very slightly at 26° . It would therefore appear that the first crystals to

form spontaneously from a mixture containing 75 per cent. benzyaniline and 25 per cent. azobenzene consist of a mixture of pure benzyaniline and mixed crystals containing 35 per cent. azobenzene with 65 per cent. benzyaniline.

5. Mixture containing 83.5 per cent. benzyaniline; 16.5 per cent. azobenzene.—This mixture also was placed in the U-tube at 70° and stirred as it cooled from this temperature to 18° in 3½ hours. A slight shower commenced at 18°, and was immediately separated from the rest of the liquid. The crystals thus obtained showed some sign of the colour of the azobenzene, and examined in capillary tubes began to melt at 26°. They therefore probably contain some proportion of the mixed crystals of composition 35 per cent. azobenzene, 65 per cent. benzyaniline. The experiment was repeated again in the same way, but in this case the first crystals separating at 18° were washed several times with benzene while still on the filter in the U-tube. When examined in capillary tubes these crystals did not melt till the temperature was raised to 35.5°, and under the microscope they appeared to be pure white in colour. Pure benzyaniline, therefore, apparently first separates spontaneously from this mixture, and if the crystals are freed from mother liquor by washing with benzene, the melting point of pure benzyaniline is attained.

6. Mixture containing 90 per cent. benzyaniline; 10 per cent. azobenzene.—This mixture was placed in the U-tube at 60° and cooled very slowly. A slight shower commenced at 20.5°, the crystals of which were easily separated by means of the vacuum pump. The crystals were small radial groups. They were washed with benzene whilst still on the filter in the U-tube, the benzene being at once drawn off with the vacuum pump. These crystals were colourless, and when placed in capillary tubes melted at 35.5°, the melting point of pure benzyaniline. If, however, the crystals were not washed with benzene before they were examined, they appeared to be yellowish in colour, and showed signs of melting at 26°. This would be accounted for by the presence of the mother liquor adhering to the crystals.

7. Mixture containing 94.74 per cent. benzyaniline; 5.26 per cent. azobenzene.—This mixture, placed in the U-tube apparatus at about 60° and cooled in the same manner, gave a shower of crystal needles and radial groups at the labile temperature, 26.5°. These were easily separated since the shower takes some time to thicken. They were washed two or three times with a few drops of benzene whilst still on the filter in the U-tube, and when placed in capillary tubes did not melt until the temperature was raised to 35.5°. They were also quite colourless, and were therefore apparently pure benzyaniline.

From these experiments it will be seen that in general, with mixtures which contain a larger amount of azobenzene than the eutectic composition, the crystals which first separate spontaneously on the supersolubility curve contain a larger percentage of azobenzene than does the original mixture. In general, for such mixtures, the supersolubility curve was found to lie above the melting-point curve. From the results obtained, therefore, with these mixtures, we see that the composition of the first crystals separating spontaneously at any point on the supersolubility curve is very approximately given by drawing a line from this point parallel to the concentration axis to meet the melting point curve. The point in which the line so drawn meets the melting point curve gives the approximate composition of the crystals which have first separated from the mixture under examination. With mixtures which contain a larger amount of benzylaniline than the eutectic composition, however, the crystals which first separate have been shown above to be pure benzylaniline.

In the case of mixtures which approximate to the eutectic composition, it has been shown that the crystals first separating are frequently a mixture of pure benzylaniline with mixed crystals of 35 per cent. azobenzene and 65 per cent. benzylaniline, the limiting composition.

Thin Sections Cut from Mixtures of Azobenzene and Benzylaniline.

An attempt was made to study the structure of a few of the solidified mixtures under the microscope. To do this thin sections were made from the mixtures that had solidified completely in glass tubes. The glass tube was broken and the solid rod of mixture removed. Discs and longitudinal sections were cut from this with a fret-saw, and then ground on ground-glass plates until they were sufficiently thin and transparent for microscopic examination.

Sections were cut in this way from the following mixtures:—

1. Mixture containing 30 per cent. azobenzene and 70 per cent. benzylaniline.—This mixture crystallised spontaneously while shaken continually in a sealed tube. When ground into thin sections this showed a large quantity of yellow rod-shaped crystals small in size, and distributed irregularly all over the sections, also some radial groups growing from centres. These are probably mixed crystals of the limiting composition, *i.e.* with 35 per cent. azobenzene and 65 per cent. benzylaniline. The rest of the section is filled up with large colourless crystals of presumably pure benzylaniline. Under the microscope these exhibit ophitic structure and extinguish in large patches all over the slide, and have probably grown at rest after the shower of mixed crystals has occurred.

This mixture was not ground into thin sections until it had been solid in a glass tube for several weeks.

2. Mixture containing 10 per cent. azobenzene and 90 per cent. benzylaniline.—This mixture also crystallised spontaneously while shaken continually in a sealed tube. This

section showed a mass of small white crystals, with small yellow crystals filling up the spaces between them. No regular arrangement could be observed, and the crystals were all more or less rod shaped.

After this section had been left for four weeks at a temperature of about 10° , it was observed that a new growth was taking place at the surface of the section. Sharply-formed thin rods could be seen quite clearly, growing out of the solid, the rods being both yellow and white in colour.

3. Mixture containing 5 per cent. azobenzene and 95 per cent. benzyaniline.—Crystallised spontaneously at rest. Sections cut from this mixture showed large, pure white crystals of benzyaniline, growing as large compact masses which extinguish together, and also as large radial groups. Small rod-shaped yellow crystals fill up the gaps.

After these sections had been kept for a few weeks at about 10° , they also showed distinct signs of segregation. Under the high power of the microscope thin rods can be seen growing up all over the surface of the sections.

4. Mixture containing 5 per cent. azobenzene and 95 per cent. benzyaniline.—Crystallised spontaneously while shaken continually. Thin sections cut from this mixture have much the appearance of the sections of (3) above, but the crystals are much smaller and arranged irregularly all over the slide.

After keeping these sections for some weeks at a low temperature, they also show thin rods growing up over their surface when examined under the high power of the microscope.

The study of the thin sections seems to indicate that, in mixtures weak in azobenzene, changes take place in the solid solutions when they are given sufficient time. It will be seen that this breaking up, or segregation, does not appear to occur in sections (1) above, but it is to be noted that these sections were not ground until the mixture had been solid for some weeks at the temperature of the room, *i.e.* about 10° . It is probable, therefore, that the change had already taken place before the section was ground, and that equilibrium had already been established between the solid solution and the benzyaniline at this temperature. The remaining sections were ground within a few hours of having solidified, so that the structures observed would correspond to equilibrium at the temperatures given by the supersolubility curve; since, presumably, sufficient time had not elapsed for them to attain equilibrium at the temperature of the room. Hence, changes begin to show themselves later in the solid section, readjustment of the components of the mixed crystals taking place until equilibrium is finally established at the ordinary air temperature.

After the lapse of three winter months these sections were all examined again under a high power. It was found that they had all undergone considerable further change, and very little of their original structure was recognisable. Sections (1), which three months before showed no sign of breaking up, had now entirely changed, and were riddled with minute crystal needles, both yellow and colourless. It was also noted that in

several of the sections the small newly formed needles were arranged in parallel positions over the surface.

Conclusion.

The results obtained in this research may be thus summarised:—

1. The freezing and melting point curves for mixtures of azobenzene and benzylaniline have been determined, and it has been shown that these substances possess a minimum or eutectic point at 26° for the mixture containing 19 per cent. azobenzene and 81 per cent. benzylaniline, and form a series of mixed crystals on one side only of the eutectic, viz., that with excess of azobenzene. This is, therefore, a limiting case of Roozeboom's Type 5, in which two substances, A and B, possess freezing and melting point curves which exhibit a minimum eutectic point, and form two series of mixed crystals, *i.e.* mixed crystals containing excess of A, and mixed crystals containing excess of B.

2. The melting point curve has been confirmed by actual analysis of the mixed crystals.

3. The supersolubility curve, or curve of spontaneous crystallisation, has been determined for these mixtures by two methods: (1) by noting the temperature at which a liquid mixture of known composition crystallises spontaneously in a sealed tube; (2) by noting the temperature at which a known liquid mixture attains its highest refractive index, and gives a dense labile shower when placed in the trough of the inverted goniometer. By these methods it has been shown that each mixture possesses a definite temperature of spontaneous crystallisation.

The supersolubility curve shows a minimum for liquids having approximately the eutectic composition, and runs approximately parallel to the freezing point curve. It crosses the melting point curve three times as shown in the diagram.

4. The nature of the mixed crystals which first separate spontaneously from any liquid mixture on the supersolubility curve has been investigated. The composition of such crystals has been determined by separating them from their mother liquor and finding their melting points.

5. A few thin sections have been ground from the solid mixtures in the neighbourhood of the eutectic, and their structures examined. These structures do not appear to be permanent, and after the lapse of some months they had completely changed, new crystal needles having appeared all over the sections. These changes, however, appear to be very gradual and to take place with change of temperature.

The analysis of these mixtures was carried out in the Balliol and Trinity Laboratory, Oxford, by permission of Messrs. Nagel and Hartley, to whom I am much indebted for their kind help and advice. I also take this opportunity of expressing my grateful thanks to Principal H. A. Miers and to Prof. Bowman for the helpful criticism and advice they have given me throughout the course of this research.

On the Improbability of a Random Distribution of the Stars in Space.

By F. W. DYSON, M.A., F.R.S.

(Received July 9, 1910.)

In a recent paper* Prof. Karl Pearson obtains the following results:—

(i) If $P = \log_{10} \pi$ when π denotes the parallax of a star, and σ_P be the standard deviation, or square root of the mean square deviation of a series of values of P from the mean; then, for a uniform distribution of stars in space, $25\sigma_P^2 = 0.5240$.

(ii) If $\bar{m}$ be the mean magnitude of all stars down to and including those of magnitude m_0 , then

$$\bar{m} = m_0 - 0.7238, \quad \text{and} \quad \sigma_m^2 = 0.5240.$$

1. The first of these results is compared with the values of $25\sigma_P^2$, obtained from a list of 72 parallaxes of stars given in Newcomb's 'The Stars: A Study of the Universe,' and with those of 163 stars given in 'Trans. Yale Univ. Observatory,' Vol. II.

For Newcomb's stars $25\sigma_P^2 = 4.22$,
and for the Yale stars, $25\sigma_P^2 = 3.11$.

The inference that these stars are not evenly distributed in space may be obtained more easily. Among the Yale stars there are ('Trans. Yale Univ. Observatory,' Vol. II, p. 205)—

17 stars with parallax $0.14''$ to $0.20''$
and 30 „ „ $0.07''$ „ $0.13''$

With a uniform distribution 8×17 , or 136 stars, may be expected to have parallaxes from $0.07''$ to $0.10''$, if there are 17 with parallaxes from $0.14''$ to $0.20''$; and a larger number than 136 between the limits $0.07''$ and $0.13''$.

* 'Roy. Soc. Proc.,' A, vol. 84, pp. 47—70.